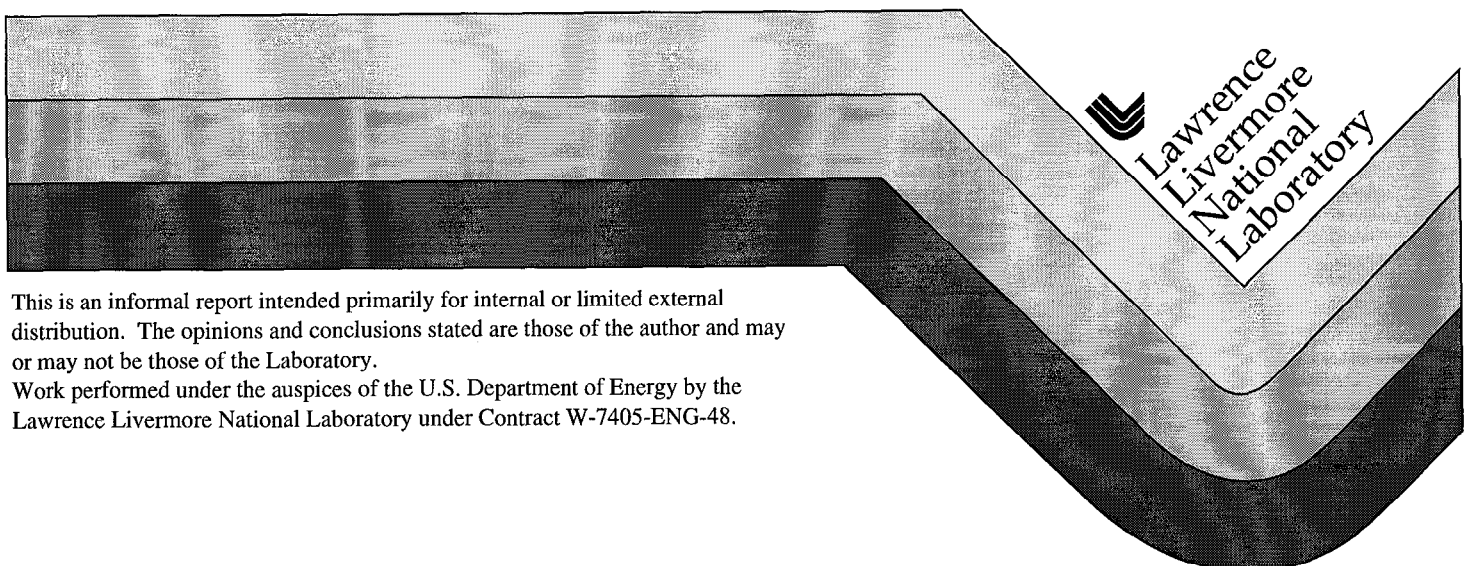


Long-Term Corrosion/Oxidation Studies Under Controlled Humidity Conditions

Greg Gdowski

October 13, 1997



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YUCCA MOUNTAIN PROJECT

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Long-Term Corrosion/Oxidation Studies Under Controlled Humidity Conditions

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YMP WBS Element 1.2.2.5.1

LLNL-YMP Metal Barrier Selection and Testing

Lawrence Livermore National Laboratory

Revision 0

TABLE OF CONTENTS

	<u>Page</u>
1.0 SCIENTIFIC INVESTIGATION PLAN.....	1
1.1 Activity Identity.....	1
1.2 Responsibilities.....	1
2.0 SCOPE, PURPOSE, AND OBJECTIVES.....	1
3.0 ACTIVITY DESCRIPTION	3
3.1 Technical and Readiness Reviews.....	4
3.2 Hold points.....	4
3.3 Equipment	5
3.4 Materials	5
3.5 Special Environmental Conditions.....	6
3.6 Special Training/Qualification Requirements.....	6
3.7 Quality Assurance Program	6
3.8 Activity Closeout	6
4.0 PRECISION AND ACCURACY	6
4.1 Calibration Requirements.....	7
4.2 Conditions which may adversely affect results	7
4.3 Sources of uncertainty and error to be controlled and measured.....	8
4.4 Standards	8
5.0 IN-PROCESS DOCUMENTATION	8
5.1 Data Recording and Data Reduction.....	8
5.2 Analysis.....	8
6.0 INTERFACES.....	9
7.0 SCHEDULE	9
8.0 TECHNICAL IMPLEMENTING PROCEDURES.....	9
9.0 SOFTWARE.....	9
10.0 SPECIAL CASES.....	10
11.0 REFERENCES	10
12.0 APPENDIX.....	10

LIST OF TABLES

	<u>Page</u>
Table 1	Minimum penetration depths measurable based on weight changes4
Table 2	Compositions of Candidate Container Materials.....11

1.0 SCIENTIFIC INVESTIGATION PLAN

This activity plan is prepared in accordance with Lawrence Livermore National Laboratory (LLNL) Yucca Mountain Project procedure 033-YMP-QP 3.0, "Scientific Investigation Control." This plan is written for Activity E-20-59, "Long Term Corrosion/Oxidation Studies under Controlled Humidity Conditions," which is part of the Scientific Investigation Plan (SIP) "Metal Barrier Selection and Testing" (SIP-CM-01, WBS #1.2.2.5.1). This activity has been determined to be quality affecting.

1.1 Activity Identity

This activity is entitled "Long Term Corrosion/Oxidation Studies under Controlled Humidity Conditions," and has been assigned the activity number E-20-59, and is part of the Long Term Abiotic Laboratory Corrosion Testing described in the SIP "Metal Barrier Selection and Testing."

1.2 Responsibilities

Key personnel responsible for performing the work in this activity are:

Technical Area Leader, Engineered Barrier System Materials, and the Principal Investigator.

The TAL responsible for this activity will be Dr. R.D. McCright.

2.0 SCOPE, PURPOSE, AND OBJECTIVES

Independent of thermal loading scenarios, the waste packages at the **potential** repository at Yucca Mountain, Nevada will be exposed to environmental conditions where there is the possibility of significant water film formation occurring on the waste packages. Water films can cause aggressive "aqueous film electrochemical corrosion" on susceptible metals or alloys. Water film formation will be facilitated when relative humidities are high, when hygroscopic salts are present on the surfaces, when corrosion products are hygroscopic, and when particles form crevices with the surfaces (capillary effect). Also certain gaseous contaminants, such as, NO_x and SO_2 , can facilitate water film formation. It should be noted that "water film" formation can occur at isolated spots (e.g. surface defects and salt particles) and need not cover the entire surface for electrochemical corrosion to occur.

This activity will characterize the long term corrosion of metal specimens at two nominal relative humidities (50 and 85%) and at 80°C. Under the low relative humidity (50%) condition, water film formation is expected to be limited and therefore aqueous film electrochemical corrosion is expected also to be limited. Under the high relative humidity (85%) condition, significant water film formation

is expected to occur under some test conditions, and subsequently aqueous film electrochemical corrosion will occur on susceptible materials.

The objective of this activity is to kinetically and mechanistically characterize the long-term corrosion and oxidation of candidate materials under constant humidity conditions. The metal specimens will be tested under a variety of conditions:

- "clean" surface - specimens that are free from significant surface contamination.
- coated with salts - specimens that are coated with salts that are characteristic of those contained in Yucca Mountain waters to simulate the effect of intermittent water contact leaving a residue or scale on the material's surface.
- in contact with a silica-based material - specimens that are in intimate contact with a silica-based material to simulate materials in contact with backfill or the eventual rock fall on the waste package.
- in contact with a cementitious material - specimens that are in contact with "invert" material to simulate the potential water film chemistry that may result from water contact with invert material or other cementitious material in the repository.

Different water film chemistries will result under each of these conditions. This will allow the characterization of the materials under various chemical and physical (creviced) conditions.

Specimens will be periodically removed from testing and will be characterized for corrosion at designated times. Total test duration is five years, possibly longer.

The results of this study will be used to assist:

- 1) in the activity "Recommendation of Container Materials (E-20-91),
- 2) in the Waste Package Performance Assessment Activities (SIP-PA-02),
- 3) in the modeling activities "Low Temperature Oxidation Model Development" (E-20-75) and "General Aqueous Corrosion Model Development" (E-20-76), and
- 4) in the Near-Field Environment and Waste Package / Repository Design effort (many of the technical issues associated with the thermal output and arrangement of waste packages in the repository greatly influence the humidity levels around the container surface and their result on container performance).

3.0 ACTIVITY DESCRIPTION

This activity will characterize the long-term corrosion of waste package candidate materials under constant temperature and humidity conditions. Two testing environments are planned. The test temperature will be nominally 80°C, and test relative humidities will be nominally 50% and 85%. All tests will be performed at atmospheric pressure. Long term is defined as times greater than 1-2 months. Kinetic and mechanistic information about the corrosion processes will be obtained.

Kinetic information will be obtained by periodically removing specimens from the test apparatus and weighing them. A decision will be made at that time as to whether the specimens will be returned to the test. Eventually the corrosion product will be removed from the specimen in order to determine the actual amount of material reacted.

There will be a sufficient number of specimens of each alloy to allow for removal and characterization of the corrosion at four designated time periods. Additional information on the reaction mechanisms will be obtained using surface analytical techniques to characterize the surface composition and structure of the corroded/oxidized metal in order to investigate variations due to different initial conditions. The surface analytical techniques will reveal complementary information on the mechanisms of oxidation and also on stability of the oxide structure. Techniques that may be employed include x-ray diffraction, microprobe analysis, Auger electron spectroscopy, x-ray photoelectron spectroscopy, infrared spectroscopy, and electron microscopy.

Nominal 2.5 cm x 5.0 cm (1" x 2") test specimens that are "clean", coated with salt, and in contact with a silica-based rock and invert material will be used. The spacers between specimens will give additional information on crevice corrosion.

Three classes of candidate metal alloys will be selected for assessment: corrosion resistant, intermediate corrosion resistant, and corrosion allowance. The corrosion resistant materials are the high nickel alloys, Alloys 625, C-22, and 825, and the dilute titanium alloy, Ti-Grade 12. The intermediate corrosion resistant materials are Monel 400 and Cu-30%Ni. The corrosion allowance materials are low alloy and carbon steels: 1018 carbon steel, cast steel, and 2.25%Cr-1%Mo steel. (See Section 3.4 "Materials" for further details.)

The primary focus of this activity will be on the corrosion allowance and intermediate corrosion resistant materials. These are the materials that are expected to be the most susceptible to the thin film aqueous electrochemical corrosion.

A conservative estimate of the minimum uniform penetration depths that can be measured in testing vary from 0.04 to 0.07 μm depending on the alloy. This estimate assumes: uniform corrosion, specimen dimensions of 2.54 cm x 5.08 cm x 0.31 cm (1"x2"x0.125") (surface area of 30.64 cm^2 (4.75 in^2)), and a weight

loss of 0.001 gm. The penetration depths are 0.07 μm for the titanium alloys (density 4.54 g/cm^3) and 0.04 μm for all the other alloys which have nearly the same densities (7.9 to 8.9 g/cm^3).

Table 1. Minimum penetration depths measurable based on weight changes (see text)

Alloy	Density (g/cm^3)	Minimum Penetration Depth Measurable (μm)
Ti (dilute alloys)	4.54	0.07
Alloy C-22	8.94	0.04
Alloy 825	8.14	0.04
Alloy 625	8.26	0.04
Alloy 400	8.83	0.04
Cu(30) - Ni(70)	8.94	0.04
Carbon steel	7.86	0.04

3.1 Technical and Readiness Reviews

No Technical or Readiness Reviews will be held for this activity

3.2 Hold points

The operation of the environmental chambers will be monitored on a continuous basis by the Principal Investigator to insure that the work is proceeding according to plan. If significant unanticipated problems arise, the Principal Investigator will inform the TAL. A joint decision will be made about the future course of action.

The progress of the test will be reported to the TAL periodically. If changes in project scope require that experimental work change direction, it is the responsibility of the TAL to communicate this to the Principal Investigator in writing.

In addition to the periodic progress reports, a yearly review of the progress of the activity is planned to ensure that the activity is proceeding according to the plan.

3.3 Equipment

The equipment used to perform the thermogravimetric analysis studies include:

Environmental chambers that can obtain the required environments and maintain them for an extend period of time.

Relative humidity: 50% and 85%

Temperature: 80°C

The chambers will be identified in the scientific notebook.

Analytical balance that is capable of measuring to 0.001 mg and has a load capacity of 200 g. Balance must be user calibrated before use. Mettler Balance AT200 or equivalent is satisfactory.

Caliber that is capable of measuring to 0.01 mm. Caliper must be user-calibrated before use.

Fowler Ultra-Cal Mark III Digital Caliper type instrument or equivalent is satisfactory.

3.4 Materials

The materials to be tested in this activity include most of the candidate metal alloys for the waste packages. For the Metal Barrier Selection and Testing Task purposes, the metallic alloy materials have been classified in three groups based on their corrosion properties: "corrosion resistant," "intermediate corrosion resistant," and "corrosion allowance." The "corrosion resistant" materials are the high nickel alloys, Alloys C-22, C-4, 625, G-3, and 825, and the dilute titanium alloys, Ti-Grades 12 and 16. The "intermediate corrosion resistant" materials are Monel 400 and Cu-30%Ni. The "corrosion allowance" materials are low alloy and carbon steels: A516 carbon steel, A27 cast steel, and 2.25%Cr-1%Mo steel. Table 2 contains the common names of the alloys, their Unified Numbering System identification number, and typical compositions.

Some of the materials are expected to have similar behavior under these test conditions; therefore, the number of material will be limited in this testing. The wrought carbon steel will be tested and not the cast steel. Alloy C-22 will be tested and not alloy C-4. Alloy G-3 will not be tested since its corrosion properties are expected to be intermediate between Alloys 825 and 625. Only one of the titanium alloys will be tested.

All the materials to be tested in this activity are commercially available metal alloys, except for the newly developed Ti-Grade 16. However, Ti-Grade 16 is a dilute titanium alloy (0.05 wt.% Pd) and is expected to have

corrosion properties similar to the higher Pd content Ti-Grade 7 (0.2 wt.% Pd) under most conditions, but at much less cost. Mechanical properties of Ti-Grade 16 are expected to be similar to those of commercial purity titanium (Ti-Grade 2).

Test specimens will be purchased commercial grade. The scientific notebook will contain the information on each metal alloy heat number, composition, and metallurgical condition. Otherwise the scientific notebook will reference the location of such information.

3.5 Special Environmental Conditions

The tests will be performed in laboratory air. Relative humidities will be controlled at 50 and 85%, and the test temperature will be 80°C. All testing will be performed at atmospheric pressure.

3.6 Special Training/Qualification Requirements

Qualifications of the Principal Investigator(s) and technicians are specified by the TAL. Only personnel trained to appropriate quality procedures and any other procedures of the Yucca Mountain Site Characterization Project will be allowed to participate in this activity.

3.7 Quality Assurance Program

This activity is to be conducted in support of "Metal Barrier Selection and Testing," as outlined in CN SIP-CM-01, Rev. 3. The study will be conducted subject to the provisions of applicable quality assurance procedures. Specific records are generated by these quality procedures; these records are the "de facto" evidence of selection and use of the procedures.

3.8 Activity Closeout

The final product of this activity will be a LLNL UCRL report documenting all results. Supporting documentation such as scientific notebooks and technical review comments will be retained by the responsible individual until the document package is transferred to the LLNL/YMP Local Records Center at the conclusion of the activity.

4.0 PRECISION AND ACCURACY

There are two categories of measurement and analysis for this activity: the test parameters, and specimen characterization both before and after testing. During testing the temperature and relative humidity of the environment will be monitored continuously. For the purposes of this testing, the test apparatus (humidity chamber) feedback control will be used to control temperature and

humidity. Periodic monitoring and recording of the temperature and humidity readout of the apparatus will be performed.

Specimen characterization will require the use of a caliper and an analytical balance. The caliper (see equipment) is capable of measuring to 0.001 in or 0.01 cm with an accuracy of ± 0.0005 in or 0.005 cm. The analytical balance (see equipment) is capable of measuring to 0.0001 g with an accuracy of ± 0.0001 g. Conservatively, uniform penetration depths of 0.1 μm can be determined with these measurements.

Post-test analysis of a test specimen will include a characterization of the surface oxidation layer. Analytical techniques could include, but are not limited to x-ray diffraction, Auger electron spectroscopy, microprobe analysis, electron microscopy, infrared spectroscopy, and x-ray photoelectron spectroscopy. The exact post-test analyses used will depend on the condition of the as-exposed specimens and will be indicated in the appropriate scientific notebooks.

4.1 Calibration Requirements

The instruments for measuring and weighing the test specimens will be user calibrated before using; the expected instruments are calipers and an analytical balance. Calibration will be performed with NIST traceable gage blocks and weights. Calibration will be documented either in the scientific notebook or on electronic media.

Temperature and humidity sensors that have been calibrated to NIST traceable standards will also be emplaced in the chambers. These sensors will serve two purposes: 1) as a check on the chamber control sensors and 2) to monitor the uniformity of conditions within the chamber. The independent sensors can be removed from the chambers and calibrated when necessary.

Since this is a long-term continuous test and removing the chamber control sensors would cause an interruption of the test, the sensors will not be required to be calibrated unless the apparatus operator determines that they are malfunctioning. An indication of malfunctioning may be significant difference in the readings between an independent sensor that has been recently calibrated.

4.2 Conditions which may adversely affect results

Any occurrence which results in the chamber temperature falling below the dew point could adversely affect the results. This would result in water condensation, which would affect the corrosion processes. Administrative procedures will be employed to ensure that the relative humidity and temperature are at acceptable values when access into the chamber is required.

Loss of power to the chamber may or may not result in condensation of water within the chamber. Any loss of power will be noted in the scientific notebook.

4.3 Sources of uncertainty and error to be controlled and measured

Any test measurement from a single specimen of a specific alloy may give anomalous results, therefore multiple specimens of a specified alloy will be used to ensure consistency.

4.4 Standards

The standards to be followed or used for guidance are listed below.

ASTM G 46-94, "Guide for Examination and Evaluation of Pitting Corrosion"

ASTM G 1-90, "Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens"

ASTM G 50-76 (1992), "Practice for Conducting Atmospheric Corrosion Tests on Metals"

5.0 IN-PROCESS DOCUMENTATION

Documentation to be generated during the conduct of this activity will include scientific notebooks and may also include data record sheets, raw data, progress reports and the final report.

After completion of the activity, a LLNL UCRL report will be written. Interim LLNL UCRL reports may also be written if deemed appropriate.

5.1 Data Recording and Data Reduction

Relative humidity and temperature data will be recorded manually into the scientific notebook or on electronic media.

Specimens will be measured and weighed before and after testing. Data recording and reduction will be done through the use of scientific notebooks, and electronic databases or spreadsheets.

5.2 Analysis

Analysis of the data will include a graphical analysis of the data in order to determine a functional form of the corrosion rate (e.g. linear or parabolic). The corrosion product formed will be characterized by surface analytical techniques in order to determine the composition and

structure of the corrosion product formed. This analysis will aid in determining the corrosion mechanisms.

6.0 INTERFACES

The information obtained in this activity will assist activities in the following technical areas:

- 1) Metal Barrier Selection and Testing (SIP-CM-01)
R.D. McCright, TAL, Metal Barrier Selection and Testing
- 2) Waste Package Performance Assessment activities (SIP-PA-2)
W. Halsey, TAL, Performance Assessment

After initiation of the experimental work, progress reports from this activity will be sent to TALs identified with the above SIP and activities. If deemed appropriate, meetings of cognizant PIs to discuss the activity's results will be conducted.

7.0 SCHEDULE

Testing will begin in FY97 and continue for at least the next five years. Specimens will be removed periodically for analysis. The specimens are independently removable with minimum disruption of the testing.

8.0 TECHNICAL IMPLEMENTING PROCEDURES

There are no Technical Implementing Procedures (TIPs) planned for the performance of this activity.

9.0 SOFTWARE

The commercial software that will be utilized in this activity are:

Igor (Wavemetrics) or similar programs for graphing and data analysis.

Excel (Microsoft) or similar spreadsheet and graphing programs for displaying ICF control and process parameters on a monitor.

Any software that will be used for analysis of the test data will be identified and discussed in the activity's Scientific Notebook.

10.0 SPECIAL CASES

No subcontractors are involved in this activity.

11.0 REFERENCES

ASTM G 46-94, "Guide for Examination and Evaluation of Pitting Corrosion"

ASTM G 1-90, "Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens"

ASTM G 50-76 (1992), "Practice for Conducting Atmospheric Corrosion Tests on Metals"

12.0 APPENDIX

There are no appendices.

Table 2. Compositions of Candidate Container Materials.

UNS number	Common or Commercial Name	ASTM Number	Nominal Composition (weight %)
N08825	Alloy 825, Incoloy 825	B 424 (plate)	Ni 38.0-46.0; Cr 19.5-23.5; Mo 2.5-3.5; Fe balance; Cu 1.5-3.0; Ti 0.6-1.2; Mn 1.0 max; C 0.05 max; Si 0.5 max; S 0.03 max; Al 0.2 max
N06030	Alloy G-30, Hastelloy G-30	B 582 (plate)	Ni balance; Cr 28.0-31.5; Mo 4.0-6.0; Fe 13.0-17.0; W 1.5-4.0; Co 5.0 max; Cu 1.0-2.4; Nb+Ta 0.3-1.5; Mn 1.5 max; C 0.03 max; Si 0.8 max; S 0.02 max; P 0.04 max
N06625	Alloy 625 Inconel 625	B 443 (plate)	Ni balance; Cr 20.0-23.0; Mo 8.0-10.0; Fe 5.00 max; Cb 3.15-4.15; Al 0.40 max; C 0.10 max; Mn 0.50 max; P 0.015 max; S 0.015 max; Si 0.50 max; Ti 0.40 max
N06455	Alloy C-4, Hastelloy C-4	B 575 (plate)	Ni balance; Cr 14.0-18.0; Mo 14.0-17.0; Fe 3.0 max; Co 2.0 max; Mn 1.0 max; C 0.015 max; Si 0.8 max; Ti 0.7 max; S 0.03 max; P 0.04 max
N06022	Alloy C-22, Hastelloy C-22	B 575 (plate)	Ni balance; Cr 20.0-22.0; Mo 12.5-14.5; Fe 2.0-6.0; W 2.5-3.5; Co 2.5 max; Mn 0.5 max; C 0.015 max; Si 0.8 max; V 0.35 max; S 0.02 max; P 0.02 max
R53400	Ti-Grade 12	B 265 Grade 12	Ni 0.6-0.9; Mo 0.2-0.4; N 0.03 max; C 0.08 max; H 0.015 max; Fe 0.3 max; O 0.25 max; Ti balance
none to date	Ti-Grade 16	none to date	0.05 Pd; Ti balance

Table 3.4.1. Compositions of Candidate Container Materials (cont'd).

UNS number	Common or Commercial Name	ASTM Number	Nominal Composition (weight %)
N04400	Alloy 400, Monel 400	B 127 (plate)	Ni 63.0 min; Cu 28.0-34.0; Fe 2.5 max; Mn 2.0 max; C 0.03 max; Si 0.5 max; S 0.024 max
C71500	70-30 copper-nickel, CDA 715	B 171 (plate)	Ni 29.0-33.0; Cu balance; Mn 1.0 max; Pb 0.02 max; Fe 0.4-1.0; Zn 0.5 max; C 0.05 max; P 0.02 max; S 0.02 max
K01800	1018 Carbon Steel	A 516 (Grade 55)	C 0.18 max; Mn 0.55-0.98; P 0.035 max; S 0.04 max; Si 0.13-0.45; Fe remainder
J02501	Centrifugally Cast Steel	A 27 (Grade 70-40)	C 0.25 max; Mn 1.2 max; P 0.050 max; S 0.060 max; Si 0.80 max; Fe remainder
K21590	2.25Cr - 1Mo Alloy Steel	A 387 (Grade 22)	C 0.15 max; Mn 0.3-0.6; P 0.035 max; S 0.035 max; Si 0.5 max; Cr 2.00-2.50; Mo 0.90-1.10; Fe remainder